Electroless deposition of Pd–Ni–P films from the polyligand pyrophosphate solutions

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Palladium-nickel-phosphorous alloys have high corrosion resistance, good solderability, wear resistance and hardness, low resistance transfer. Due to these properties Pd–Ni–P films are applied as finishing coatings in the production of different electronic devices instead of gold, as a sublayer for the deposition of palladium thin films, as the diffusion barrier at the assembly of electronic circuit boards and optoelectronic devices. As a rule, solutions for electroless Pd–Ni–P deposition contain ammonium, ethylenediamine (En), ethylenediamine tetraacetate or their mixture as the ligands. Sodium hypophosphite and potassium boronhydride are used as the reducing agents. Great difference between the values of Pd^{2+}/Pd^0 and Ni^{2+}/Ni^0 standard electrode potentials and easy reduction of much more electropositive Pd(II) stipulate the predominant content of palladium in Pd–Ni–P alloys and a low stability of solutions. Therefore, to diminish the gap between redox potentials of palladium and nickel and to retard Pd(II) reduction in the solution bulk it is necessary to select ligands or ligands mixtures providing the formation of stable complexes with palladium. That can be achieved in case of K_s $(PdL_xM_y) >> K_s$ (NiL_xM_y), where K_s is the stability constant and L and M are ligands, *x* and *y* can be varied from 2 to 4.

The purpose of this work was to develop the composition of stable solution for electroless Pd–Ni–P films deposition containing three types of ligands (pyrophosphate ions, ammonium and En), the investigation of peculiarities of joint Ni(II) and Pd(II) electroless reduction in polyligand solution, the analysis of elemental and phase composition of the coatings obtained and evaluation of their protective properties.

Stable electrolyte with pH 10.2 containing pyrophosphate ions, ammonium and En have been developed. The electrolyte allowed us to deposit coatings with the rate 1.5 μm/h with nickel, palladium and phosphorous content equal to 77.0, 12.8 and 10.2 at.%, accordingly. Freshly deposited coatings included Ni_3P, Pd_7P_3 crystalline phases and amorphous palladium. At thermal treatment of Pd–Ni–P coatings crystalline phase of solid solution of palladium in nickel with palladium content equal to 8 at.% appeared.

In the result of voltammetric study of cathodic processes occurred on copper electrodes in polyligand pyrophosphate solutions it was established that the joint reduction of Ni(II) *и* Pd(II) proceeded with the depolarization effect in comparison with Ni(II) individual reduction but with the effect of overpolarization in comparison with Pd(II) individual reduction in the solutions with the analogous composition. The results of voltammetric experiments conducted with nickel working electrode modeling the later stages of Ni–Pd–P films deposition have shown that the joint Ni(II) and Pd(II) reduction proceeded with the effect of depolarization in comparison with individual Ni(II) and Pd(II) reduction. These results explain high nickel content in the alloy.

Pd–Ni–P, Ni–P, Pd–P coatings 1 μm thick deposited from solutions with the identical composition were tested for corrosion by the weight losses of the samples in the chamber of heat and moisture and in solution containing 3 mass. % NaCl and citrate buffer with pH 6. It was found that these coatings had no sufficient differences in their corrosion stability.